

# 10

## Germanium, Tin and Lead

### 10.1 Introduction

Germanium was predicted as the missing element of a triad between silicon and tin by J. A. R. Newlands in 1864, and in 1871 D. I. Mendeleev specified the properties that “ekasilicon” would have (p. 29). The new element was discovered by C. A. Winkler in 1886 during the analysis of a new and rare mineral argyrodite,  $\text{Ag}_8\text{GeS}_6$ ;<sup>(1)</sup> he named it in honour of his country, Germany.<sup>†</sup> By contrast, tin and lead are two of the oldest metals known

<sup>1</sup> M. E. WEEKS, *Discovery of the Elements*, 6th edn., Journal of Chemical Education Publ. 1956, 910 pp. Germanium, pp. 683–93; Tin and lead, pp. 41–7.

<sup>†</sup> The astonishing correspondence between the predicted and observed properties of Ge (p. 29) has tempted later writers to overlook the fact that Winkler thought he had discovered a metalloid like As and Sb and he originally identified Ge with Mendeleev’s (incorrectly) predicted “eka-stibium” between Sb and Bi; Mendeleev himself thought it was “eka-cadmium”, which he had (again incorrectly) predicted as a missing element between Cd and Hg. H. T. von Richter thought it was “eka-silicon”; so did Lothar Meyer, and they proved to be correct. This illustrates the great difficulties encountered by chemists working only 100 y ago, yet three decades before the rationale which stemmed from the work of Moseley and Bohr.

to man and both are mentioned in early books of the Old Testament. The chemical symbols for the elements come from their Latin names *stannum* and *plumbum*. Lead was used in ancient Egypt for glazing pottery (7000–5000 BC); the Hanging Gardens of Babylon were floored with sheet lead to retain moisture and the Romans used lead extensively for water-pipes and plumbing; they extracted some 6–8 million tonnes in four centuries with a peak annual production of 60 000 tonnes. Production of tin, though equally influential, has been on a more modest scale and dates back to 3500–3200 BC. Bronze weapons and tools containing 10–15% Sn alloyed with Cu have been found at Ur, and Pliny described solder as an alloy of Sn and Pb in AD 79.

Germanium and Sn are non-toxic (like C and Si). Lead is now recognized as a heavy-metal poison;<sup>(2)</sup> it acts by complexing with oxo-groups

<sup>2</sup> J. J. CHISHOLM, Lead poisoning, *Scientific American* 224, 15–23 (1971). Reprinted as Chap. 36 in *Chemistry in the Environment*, Readings from *Scientific American*, pp. 335–43. W. H. Freeman, San Francisco, 1973. See also R. M. HARRISON and D. P. H. LAXEN, *Lead Pollution*, Chapman and Hall, London, 1981, 175 pp; T. C. HUTCHINSON and K. N. MEEMA (eds.), *Lead, Mercury, Cadmium and* (ctd.)

in enzymes and affects virtually all steps in the process of haem synthesis and porphyrin metabolism. It also inhibits acetylcholine-esterase, acid phosphatase, ATPase, carbonic anhydrase, etc. and inhibits protein synthesis probably by modifying transfer-RNA. In addition to O complexation (in which it resembles  $Tl^I$ ,  $Ba^{II}$  and  $Ln^{III}$ ),  $Pb^{II}$  also inhibits SH enzymes (though less strongly than  $Cd^{II}$  and  $Hg^{II}$ ), especially by interaction with cysteine residues in proteins. Typical symptoms of lead poisoning are cholic, anaemia, headaches, convulsions, chronic nephritis of the kidneys, brain damage and central nervous-system disorders. Treatment is by complexing and sequestering the Pb using a strong chelating agent such as edta,  $\{-CH_2N(CH_2CO_2H)_2\}_2$ , or BAL i.e. British anti-Lewisite,  $HSCH_2CH(SH)CH_2OH$ .

## 10.2 The Elements

### 10.2.1 Terrestrial abundance and distribution

Germanium and Sn appear about half-way down the list of elements in order of abundance in crustal rocks, together with several other elements in the region of 1–2 ppm:

Element	Br	U	<b>Sn</b>	Eu	Be	As
PPM	2.5	2.3	<b>2.1</b>	2.1	2	1.8
Order	46	47	<b>48</b>	=48	50	51

Element	Ta	<b>Ge</b>	Ho	Mo	W	Tb
PPM	1.7	<b>1.5</b>	1.4	1.2	1.2	1.2
Order	52	<b>53</b>	54	55	=55	=55

Germanium minerals are extremely rare but the element is widely distributed in trace amounts (like its neighbour Ga). Recovery has been achieved from coal ash but is now normally from the flue dusts of smelters processing Zn ores.

*Arsenic in the Environment*, SCOPE 31, Wiley, Chichester, 1987, 384 pp.

Tin occurs mainly as cassiterite,  $SnO_2$ , and this has been the only important source of the element from earliest times. Julius Caesar recorded the presence of tin in Britain, and Cornwall remained the predominant supplier for European needs until the present century (apart from a minor flourish from Bohemia between 1400 and 1550).<sup>(3)</sup> Today (1990s) world production approaches 200 000 tonnes per annum (see next section), of which the UK contributes less than 1%.<sup>(4)</sup>

Lead (13 ppm) is by far the most abundant of the heavy elements, being approached amongst these only by thallium (8.1 ppm) and uranium (2.3 ppm). This abundance is related to the fact that 3 of the 4 naturally occurring isotopes of lead (206, 207 and 208) arise primarily as the stable end products of the natural radioactive series. Only  $^{204}Pb$  (1.4%) is non-radiogenic in origin. The variation in isotopic composition of Pb with its origin also accounts for the variability of atomic weight and the limited precision with which it can be quoted (p. 19). The most important Pb ore is the heavy black mineral galena,  $PbS$ . Other ore minerals are anglesite ( $PbSO_4$ ), cerussite ( $PbCO_3$ ), pyromorphite ( $Pb_5(PO_4)_3Cl$ ) and mimetesite ( $Pb_5(AsO_4)_3Cl$ ). Some 25 other minerals are known but are not economically important; all contain  $Pb^{II}$  in contrast to tin minerals which are invariably  $Sn^{IV}$  compounds. Lead ores are widely distributed and commercial deposits are worked in over fifty countries. Primary production (from mines) was 3.3 million tonnes (as Pb) in 1991 of which four-fifths came from the half dozen main producers: Australia 17.4%, USA 14.3%, the former Soviet Union 13.8%, China 9.6%, Canada 8.3% and Peru 6.0%.<sup>(4)</sup> Secondary production (from the resmelting of scrap) produces a further 5.6 Mtpa i.e. nearly two-thirds of the world's supply in 1991. The average price in 1992 was £306.4/tonne (\$542/t).

<sup>3</sup> R. D. PENHALLURICK, *Tin in Antiquity*, Institute of Metals Publication, 1986, 271 pp.

<sup>4</sup> A. MACMILLAN (ed.) *Base Metals Handbook*, Woodhead Publ., Cambridge, 1993 (loose leaf). See also refs. 6 and 9.

### 10.2.2 Production and uses of the elements

Recovery of Ge from flue dusts is complicated, not only because of the small concentration of Ge but also because its amphoteric properties are similar to those of Zn from which it is being separated.<sup>(5)</sup> Leaching with  $\text{H}_2\text{SO}_4$ , followed by addition of aqueous NaOH, results in the coprecipitation of the 2 elements at pH  $\sim 5$  and enrichment of Ge from  $\sim 2$  to 10%:  $\text{GeO}_2$  begins to precipitate at pH 2.4, is 90% precipitated at pH 3, and 98% precipitated at pH 5.  $\text{Zn}(\text{OH})_2$  begins to precipitate at pH 4 and is completely precipitated at pH 5.5. The concentrate is heated with  $\text{HCl}/\text{Cl}_2$  to drive off  $\text{GeCl}_4$ , bp  $83.1^\circ$  (cf.  $\text{ZnCl}_2$ , bp  $756^\circ$ ). After further fractionation of  $\text{GeCl}_4$ , hydrolysis affords purified  $\text{GeO}_2$ , which can be slowly reduced to the element by  $\text{H}_2$  at  $\sim 530^\circ$ . Final purification for semiconductor-grade Ge is effected by zone refining. World production of Ge in 1991 was 80 000 kg (80 tonnes), about 10% less than a decade earlier. The largest use is in transistor technology and, indeed, transistor action was first discovered in this element (p. 331). This use is now diminishing somewhat whilst that in optics is growing — Ge is transparent in the infrared and is used in infrared windows, prisms and lenses. Magnesium germanate is a useful phosphor, and other small-scale applications are in special alloys, strain gauges and superconductors. Despite its spectacular increase in availability during the past few decades from a laboratory rarity to a general article of commerce Ge and its compounds are still relatively expensive. Zone-refined Ge was quoted at \$850 per kg in 1991 and  $\text{GeO}_2$  at \$500 per kg.

The ready reduction of  $\text{SnO}_2$  by glowing coals accounts for the knowledge of Sn and its alloys in the ancient world. Modern technology uses a reverberatory furnace at  $1200\text{--}1300^\circ$ .<sup>(6)</sup> The main chemical problem in reducing  $\text{SnO}_2$  comes

from the presence of Fe in the ores which leads to a hard product with unacceptable properties. Reference to Ellingham-type diagrams of the sort shown on p. 308 shows that  $-\Delta G(\text{SnO}_2)$  is very close to that for  $\text{FeO}/\text{Fe}_3\text{O}_4$  and only about  $80\text{ kJ mol}^{-1}$  above the line for reducing FeO to Fe at  $1000\text{--}2000^\circ$ . It is therefore essential to reduce cassiterite/iron oxide ores at an oxygen pressure sufficiently high to prevent extensive reduction to Fe. This is achieved in a two-stage process, the impure molten Sn from the initial carbon reduction being stirred vigorously in contact with atmospheric  $\text{O}_2$  to oxidize the iron — a process that can be effected by “poling” with long billets of green wood — or, alternatively, by use of steam or compressed air. The price of tin was formerly regulated by The International Tin Council, but the market became progressively less stable and the suspension of buffer stock interventions in October 1985 precipitated an immediate collapse in the market from which it has not yet recovered. The ITC was superseded by The Association of Tin Producing Countries which attempts to limit production by the member countries. In 1991 there was an excess of tin on the world market for the 11th successive year and primary production was limited to 95 850 tonnes (Malaysia 29.8%, Indonesia 29.6%, Thailand 17.9%, Bolivia 13.2%, Australia 7.2%, Zaire 1.4%, Nigeria 0.9%). Additional production by China (43 000 t), the former USSR (13 500 t) and other countries brought the primary production of Sn in concentrates in 1991 to 196 700 tonnes. Prices hovered around \$5700 per tonne, about half that of a few years earlier.<sup>(7,8)</sup> The many uses of metallic tin and its alloys are summarized in the Panel overleaf.

Lead is normally obtained from PbS. This is first concentrated from low-grade ores by froth flotation then roasted in a limited supply of air

<sup>5</sup> Kirk-Othmer *Encyclopedia of Chemical Technology* 4th edn. 12, 540–55 (1994). Germanium and germanium compounds.

<sup>6</sup> Kirk-Othmer *Encyclopedia of Chemical Technology* 3rd edn. 23, 18–42 (1983), Tin and tin alloys; 42–77, Tin compounds.

<sup>7</sup> *Minerals year book, Vol. 1: Metals and Minerals*, 1991, US Dept. of the Interior, Bureau of Mines. Ge pp. 649–54; Sn pp. 1591–612, Pb pp. 873–910.

<sup>8</sup> R. WOLFF, *Tin Market Report*, Metal Bulletin Books Ltd., Worcester Park, Surrey, 1991.

### Uses of Metallic Tin and Its Alloys

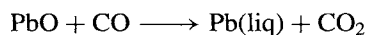
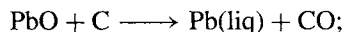
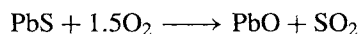
Because of its low strength and high cost, Sn is seldom used by itself but its use as a coating, and as alloys, is familiar in a variety of domestic and technological applications. Tin-plate accounts for almost 27% of tin used — it provides a non-toxic corrosion-resistant cover for sheet steel and can be applied either by hot dipping in molten Sn or more elegantly and controllably by electrolytic tinning. The layer is typically 0.4–25  $\mu\text{m}$  thick. In addition to extensive use in food packaging, tin-plate is used increasingly for distributing beer and other drinks. In the USA alone 35 000 million of the 130 000 million drink cans sold annually are tin-plate, the rest being Al: this is a staggering per capita consumption of 500 pa.

The main alloys of tin together with an indication of the percentage of total Sn production for these alloys in the USA (1991) are:

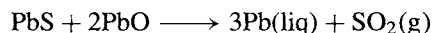
Solder (37%)	(Sn/Pb) typically containing 33% Sn by weight but varying between 2–63% depending on use; sometimes Cd, Ga, In or Bi are added for increased fusibility.
Bronze (7%)	(Cu/Sn) typically 5–10% Sn often with added P or Zn to aid casting and impart superior elasticity and strain resistance. Gun metal is ~85% Cu, 5% Sn, 5% Zn and 5% Pb. Coinage metal and brass also often contain small amounts of Sn. World production of bronzes approaches 500 000 tonnes pa.
Babbitt (2%)	(heavy duty bearing metal introduced by I. Babbitt in 1839). The two main compositions are 80–90% Sn, 0–5% Pb, 5% Cu; and 75% Pb, 12% Sn, 13% Sb, 0–1% Cu. They have the characteristics of a hard compound embedded in a soft matrix and are used mainly in railway wagons, diesel locomotives, etc.
Pewter (3%)	(90–95% Sn, 1–8% Sb, 0.5–3% Cu); a decorative and servicable alloy that can be cast, bent, spun or formed into any shape; it is much used for coffee and tea services, trays, plates, jugs, tankards, candelabra, bowls and trophies. A related alloy of 90–95% Sn with Pb and other elements is highly prized and much used for organ pipes because of its tonal qualities, e.g. the Royal Albert Hall organ in London has 10 000 pipes containing some 150 tonnes Sn.

Other specialized uses of Sn and its alloys are as type metal, as the molten-metal bath in the manufacture of float glass and as the alloy  $\text{Nb}_3\text{Sn}$  in superconducting magnets. The many industrial and domestic uses of tin compounds are discussed in later sections; these compounds account for about 15% of the tin produced worldwide.

to give  $\text{PbO}$  which is then mixed with coke and a flux such as limestone and reduced in a blast furnace:<sup>(9)</sup>



Alternatively, the carbon reduction can be replaced by reduction of the roasted ore with fresh galena:



<sup>9</sup> *Kirk-Othmer Encyclopedia of Chemical Technology* 4th edn. 15, 69–113 (1995), Lead; 113–32, Lead alloys; 132–58, Lead compounds.

In either case the Pb contains numerous undesirable metal impurities, notably Cu, Ag, Au, Zn, Sn, As and Sb, some of which are clearly valuable in themselves. Copper is first removed by liquation: the Pb bullion is melted and held just above its freezing point when Cu rises to the surface as an insoluble solid which is skimmed off. Tin, As and Sb are next removed by preferential oxidation in a reverberatory furnace and skimming off the oxides; alternatively, the molten bullion is churned with an oxidizing flux of molten  $\text{NaOH}/\text{NaNO}_3$  (Harris process). The softened Pb may still contain Ag, Au and perhaps Bi. Removal of the first two depends on their preferential solubility in Zn: the mixed metals are cooled slowly from 480° to below 420° when the Zn (now containing nearly all the Ag and Au) solidifies as a crust which is skimmed off; the

### Uses of Lead Alloys and Chemicals

Although much lead is used as an inert material in cast, rolled or extruded form, a far greater tonnage is consumed as alloys. Its major application is in storage batteries where an alloy of 91% Pb, 9% Sb forms the supporting grid for the oxidizing agent ( $\text{PbO}_2$ ) and the reducing agent (spongy Pb).<sup>(10)</sup> Over 70% of this Pb is recovered and recycled. In addition, its use (with Sn) in solders, fusible alloys, bearing metals (babbitt) and type metals has been summarized on p. 370. Other mechanical as distinct from chemical applications are in ammunition, lead shot, lead weights and ballast.

The pattern of chemical usage of Pb compounds in a particular country depends very much on whether organolead compounds are allowed as antiknock additives in petrol for cars (gasoline for automobiles). In a growing number of developed countries such additives are considered to be wasteful, dangerous and unnecessary and environmental legislation is gradually achieving the elimination of  $\text{PbEt}_4$  and  $\text{PbMe}_4$  as antiknocks.<sup>(2)</sup> The presence of Pb additives in petrol also interferes with the catalytic converters that are being developed to reduce or eliminate CO,  $\text{NO}_x$  and hydrocarbons from exhaust fumes, and this has likewise encouraged the change to other antiknocks.

World production of mined lead was 3 331 000 tonnes in 1991 and a further 5 558 000 tonnes was refined by reprocessing. In the same year US consumption of Pb in metal products was 1 125 000 tonnes (including 967 000 tonnes in storage batteries). In addition, some 57 250 tonnes of other oxides and 29 750 tonnes of miscellaneous Pb-containing products were consumed. The US market price of Pb dropped from \$1.05/kg in 1990 to \$0.40/kg in 1993 due in part to the collapse in use of  $\text{PbEt}_4$  in petrol.

Lead pigments are widely used as rust-inhibiting priming paints for iron and steel. Red lead ( $\text{Pb}_3\text{O}_4$ ) is the traditional primer but  $\text{Ca}_2\text{PbO}_4$  is finding increasing use, particularly for galvanized steel. Lead chromate,  $\text{PbCrO}_4$ , is a strong yellow pigment extensively used in yellow paints for road markings and as an ingredient (with iron blues) in many green paints and coloured plastics. Other pigments include  $\text{PbMoO}_4$  (red-orange), litharge  $\text{PbO}$  (canary yellow), and white lead,  $\sim 2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . Lead compounds are also used for ceramic glazes, e.g.  $\text{PbSi}_2\text{O}_5$  (colourless), in crown glass manufacture, and as polyvinylchloride plastic stabilizers, e.g. "tribasic lead sulfate",  $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ . See also p. 386.

excess of dissolved Zn is then removed either by oxidation in a reverberatory furnace, or by preferential reaction with gaseous  $\text{Cl}_2$ , or by vacuum distillation. Final purification (which also removes any Bi) is by electrolysis using massive cast Pb anodes and an electrolyte of acid  $\text{PbSiF}_6$  or a sulfamate;<sup>(10)</sup> this yields a cathode deposit of 99.99% Pb which can be further purified by zone refining to <1 ppm impurity if required. Total world production figures and the current price were given at the end of the preceding section, and the various uses for lead alloys and chemicals are summarized in the Panel.

### 10.2.3 Properties of the elements

The atomic properties of Ge, Sn and Pb are compared with those of C and Si in Table 10.1. Trends noted in previous groups are again apparent. The pairwise similarity in the ionization energies of Si and Ge (which can be related to the filling of the  $3d^{10}$  shell) and of Sn and Pb

(which is likewise related to the filling of the  $4f^{14}$  shell) are notable (Fig. 10.1). Tin has more stable isotopes than any other element (why?) and one of these,  $^{119}\text{Sn}$  (nuclear spin  $\frac{1}{2}$ ), is particularly valuable both for nmr experiments<sup>(11)</sup> and for Mössbauer spectroscopy.<sup>(12)</sup>

Some physical properties of the elements are compared in Table 10.2. Germanium forms brittle, grey-white lustrous crystals with the diamond structure; it is a metalloid with a similar electrical resistivity to Si at room temperature but with a substantially smaller band gap. Its mp, bp and associated enthalpy changes are also lower than for Si and this trend continues for Sn and Pb which are both very soft, low-melting metals.

Tin has two allotropes: at room temperature the stable modification is white, tetragonal

<sup>10</sup> A. T. KUHN (ed.), *The Electrochemistry of Lead*, Academic Press, London, 1977, 467 pp. H. BODE, *Lead-Acid Batteries*, Wiley, New York, 1977, 408 pp.

<sup>11</sup> J. D. KENNEDY and W. MCFARLANE, in J. MASON (ed), *Multinuclear NMR*, Plenum Press, New York, 1987, Chap. 11, Si, Ge, Sn and Pb, pp. 305–33. See also B. WRACKMEYER, *Ann. Rept. NMR Spectrosc.* **16**, 73–186 (1985).

<sup>12</sup> N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, Chapman & Hall, London, 1971, 659 pp. T. C. GIBB, *Principles of Mössbauer Spectroscopy*, Chapman & Hall, London, 1976, 254 pp.

Table 10.1 Atomic properties of Group 14 elements

Property	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Electronic structure	[He]2s <sup>2</sup> 2p <sup>2</sup>	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Number of naturally occurring isotopes	2 + 1	3	5	10	4
Atomic weight	12.0107(8)	28.0855(3)	72.61(2)	118.710(7)	207.2(1)
Ionization energy/kJ mol <sup>-1</sup>	I	1086.1	786.3	761.2	708.4
	II	2351.9	1576.5	1537.0	1411.4
	III	4618.8	3228.3	3301.2	2942.2
	IV	6221.0	4354.4	4409.4	3929.3
<i>r</i> <sup>IV</sup> (covalent)/pm	77.2	117.6	122.3	140.5	146
<i>r</i> <sup>IV</sup> ("ionic"; 6-coordinate)/pm	(15) (CN 4)	40	53	69	78
<i>r</i> <sup>II</sup> ("ionic"; 6-coordinate)/pm	—	—	73	118	119
Pauling electronegativity	2.5	1.8	1.8	1.8	1.9

 **LIVE GRAPH**  
Click here to view

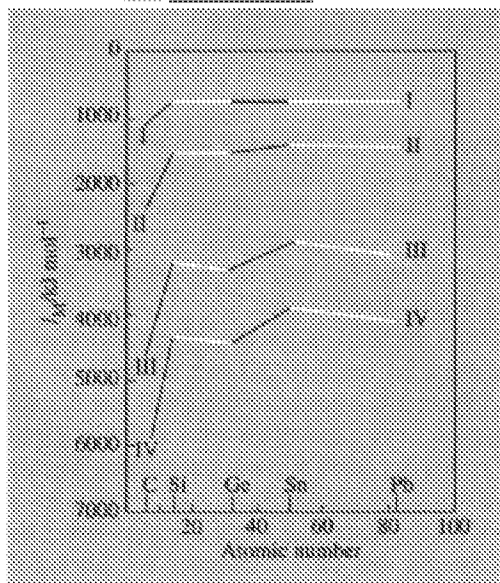


Figure 10.1 Successive ionization energies for Group 14 elements showing the influence of the 3d<sup>10</sup> shell between Si and Ge and the 4f<sup>14</sup> shell between Sn and Pb.

$\beta$ -Sn, but at low temperatures this transforms into grey  $\alpha$ -Sn which has the cubic diamond structure. The transition temperature is 13.2° but the transformation usually requires prolonged exposure at temperatures well below this.

The reverse transition from  $\alpha \rightarrow \beta$  involves a structural distortion along the *c*-axis and is remarkable for the fact that the density increases by 26% in the high-temperature form. This arises because, although the Sn–Sn distances increase in the  $\alpha \rightarrow \beta$  transition, the CN increases from 4 to 6 and the distortion also permits a closer approach of the 12 next-nearest neighbours:

Modification	$\alpha$ (grey, diamond)	$\beta$ (white, tetragonal)
Bond angles	6 at 109.5°	$\left\{ \begin{array}{l} 4 \text{ at } 94^\circ \\ 2 \text{ at } 149.6^\circ \end{array} \right.$
Nearest neighbours	4 at 280 pm	$\left\{ \begin{array}{l} 4 \text{ at } 302 \text{ pm} \\ 2 \text{ at } 318 \text{ pm} \end{array} \right.$
Next nearest neighbours	12 at 459 pm	$\left\{ \begin{array}{l} 4 \text{ at } 377 \text{ pm} \\ 8 \text{ at } 441 \text{ pm} \end{array} \right.$

A similar transformation to a metallic, tetragonal  $\beta$ -form can be effected in Si and Ge by subjecting them to pressures of  $\sim 200$  and  $\sim 120$  kbar respectively along the *c*-axis, and again the density increases by  $\sim 25\%$  from the value at atmospheric pressure. Lead is familiar as a blue-grey, malleable metal with a fairly high density (nearly 5 times that of Si and twice those of Ge and Sn, but only half that of Os and Ir).

Table 10.2 Some physical properties of Group 14 elements

Property	C	Si	Ge	Sn	Pb
MP/°C	4100	1420	945	232	327
BP/°C	—	~3280	2850	2623	1751
Density (20°C)/g cm <sup>-3</sup>	3.514	2.336 ( $\beta$ 2.905) <sup>(a)</sup>	5.323 ( $\beta$ 6.71) <sup>(a)</sup>	$\alpha$ 5.769 $\beta$ 7.265 <sup>(b)</sup>	11.342
$a_0$ /pm	356.68 <sup>(c)</sup>	543.10 <sup>(c)</sup>	565.76	$\alpha$ 648.9 <sup>(b,c)</sup>	494.9 <sup>(d)</sup>
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	—	50.6	36.8	7.07	4.81
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	—	383	328	296	178
$\Delta H_{\text{f}}$ (monatomic gas)/kJ mol <sup>-1</sup>	716.7	454	283	300.7	195.0
Electrical resistivity (20°)/ohm cm	$10^{14}$ – $10^{16}$	~48	~47	$\beta$ $11 \times 10^{-6}$	$20 \times 10^{-6}$
Band gap $E_g$ /kJ mol <sup>-1</sup>	~580	106.8	64.2	$\alpha$ 7.7, $\beta$ 0	0

(a) See text. (b)  $\beta$ -form (stable at room temperature) is tetragonal  $a_0$  583.1 pm,  $c_0$  318.1 pm.

(c) Diamond structure. (d) Face-centred cubic.

### 10.2.4 Chemical reactivity and group trends

Germanium is somewhat more reactive and more electropositive than Si: it dissolves slowly in hot concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  but does not react with water or with dilute acids or alkalis unless an oxidizing agent such as  $\text{H}_2\text{O}_2$  or  $\text{NaOCl}$  is present; fused alkalis react with incandescence to give germanates. Germanium is oxidized to  $\text{GeO}_2$  in air at red heat and both  $\text{H}_2\text{S}$  and gaseous S yield  $\text{GeS}_2$ ;  $\text{Cl}_2$  and  $\text{Br}_2$  yield  $\text{GeX}_4$  on moderate heating and  $\text{HCl}$  gives both  $\text{GeCl}_4$  and  $\text{GeHCl}_3$ . Alkyl halides react with heated Ge (as with Si) to give the corresponding organogermanium halides.

Tin<sup>(13)</sup> is notably more reactive and electropositive than Ge though it is still markedly amphoteric in its aqueous chemistry. It is stable towards both water and air at ordinary temperatures but reacts with steam to give  $\text{SnO}_2$  plus  $\text{H}_2$  and with air or oxygen on heating to give  $\text{SnO}_2$ . Dilute  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  show little, if any, reaction but dilute  $\text{HNO}_3$  produces  $\text{Sn}(\text{NO}_3)_2$  and  $\text{NH}_4\text{NO}_3$ . Hot concentrated  $\text{HCl}$  yields  $\text{SnCl}_2$  and  $\text{H}_2$  whereas hot concentrated  $\text{H}_2\text{SO}_4$  forms  $\text{SnSO}_4$  and  $\text{SO}_2$ . The occurrence of  $\text{Sn}^{\text{II}}$  compounds in these reactions is notable. By contrast, the action of hot aqueous alkali yields

hydroxostannate(IV) compounds, e.g.:



Tin reacts readily with  $\text{Cl}_2$  and  $\text{Br}_2$  in the cold and with  $\text{F}_2$  and  $\text{I}_2$  on warming to give  $\text{SnX}_4$ . It reacts vigorously with heated S and Se, to form  $\text{Sn}^{\text{II}}$  and  $\text{Sn}^{\text{IV}}$  chalcogenides depending on the proportions used, and with Te to form  $\text{SnTe}$ .

Finely divided Pb powder is pyrophoric but the reactivity of the metal is usually greatly diminished by the formation of a thin, coherent, protective layer of insoluble product such as oxide, oxocarbonate, sulfate or chloride. This inertness has been exploited as one of the main assets of the metal since early times: e.g. a temperature of 600–800° is needed to form  $\text{PbO}$  in air and Pb is widely used for handling hot concentrated  $\text{H}_2\text{SO}_4$ . Aqueous  $\text{HCl}$  does, in fact, react slowly to give the sparingly soluble  $\text{PbCl}_2$  (<1% at room temperature) and nitric acid reacts quite rapidly to liberate oxides of nitrogen and form the very soluble  $\text{Pb}(\text{NO}_3)_2$  (~50 g per 100 cm<sup>3</sup>, i.e. 1.5 M). Organic acids such as acetic acid also dissolve Pb in the presence of air to give  $\text{Pb}(\text{OAc})_2$ , etc.; this precludes contact with the metal when processing or storing wine, fruit juices and other drinks. The familiar soft metal protective caps covering the cork on quality wines is Pb-foil laminated between thin outer layers of non-toxic Sn metal to which coloured decorative finishes can be applied. Fluorine reacts at room temperatures to give  $\text{PbF}_2$  and  $\text{Cl}_2$  gives  $\text{PbCl}_2$  on heating.

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<sup>13</sup> P. G. HARRISON (ed.), *Chemistry of Tin*, Blackie, Glasgow, 1989, 461 pp.